INTERFACIAL STRUCTURE AND STRENGTH OF ADHESIVE BONDS

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An adhesive bond is a sandwich structure that has various zones within it as shown in Fig. 1. The physical and checmical properties of these various zones determine the bond strength and the durability of the bond. I hope that I'll be able to shed some light on the real properties of the interface rather than schematic properties as shown in Fig. 1 and relate the physical and chemical properties to the resultant bond strength. I will, therefore, discuss something about the oxide, the topography of the surface after it's been prepared for bonding, the thickness of the oxide, the interface, the primer and the adhesive in an actual fracture surface. The dotted line in Fig. 1 represents a hypothetical fracture line and, in fact, we find that failure does occur in all of these regions designated by the dashed line. The bond fails as the weakest regions fail.

I want to address my remarks specifically to the system aluminum 2024-T3 and with the FPL standard etch (sulfuric acid-dichromate) and a glass carrier epoxy adhesive (HT-424). When you prepare the aluminum surface with the FPL etch and look at it with a scanning electron microscope, you can see in Fig. 2 that, even though 1 mil of aluminum has been removed in the etch process, the rolling lines are still evident. However, the main feature of the surface is the very large number of etch pits of all sizes.

Based on examinations with various instruments, a representation of the cross-section of the surface of the aluminum after an FPL etch is given in Fig. 3. The surface has large etch pits of the order of 1 to 10 μm. If you expand one of these etch pits to much larger magnification, you see the large etch pit has a more or less uniform set of much smaller etch pits. And then if you expand that up again, you see the structure is somewhat as shown at the top of Fig. 3. The actual oxide film is of the order of 100 to 200 Å, as shown by ellipsometry and photoelectron emission. Scanning electron microscopy indicates that the width or the diameter of these pits is approximately 500 to 1000 Å and the depth is approximately 400 Å. I might mention that when we started this work about 2 1/2 years ago, the only study that had been done that I could find indicated that the oxide film thickness was from 6500 to 45000Å.

The chemistry of the oxide film on aluminum was elucidated with Auger spectroscopy in conjunction with sputterback etching with argon ions. As shown in Fig. 4, chemical profiles for the elements as you go through the oxide film, although semi-quantitative, are very informative. At the metal interface (dashed vertical line in Fig. 4), the oxygen peak has gone to 0; the aluminum peak, for Al^{3+} in the oxide, has gone to 0; and the metal 67 ev peak, has leveled off. At the outer oxide surface there is iron, sulphur, carbon, and the copper constituent of the alloy, but also some nickel that's supposedly not in the alloy. The copper goes through a maxi-

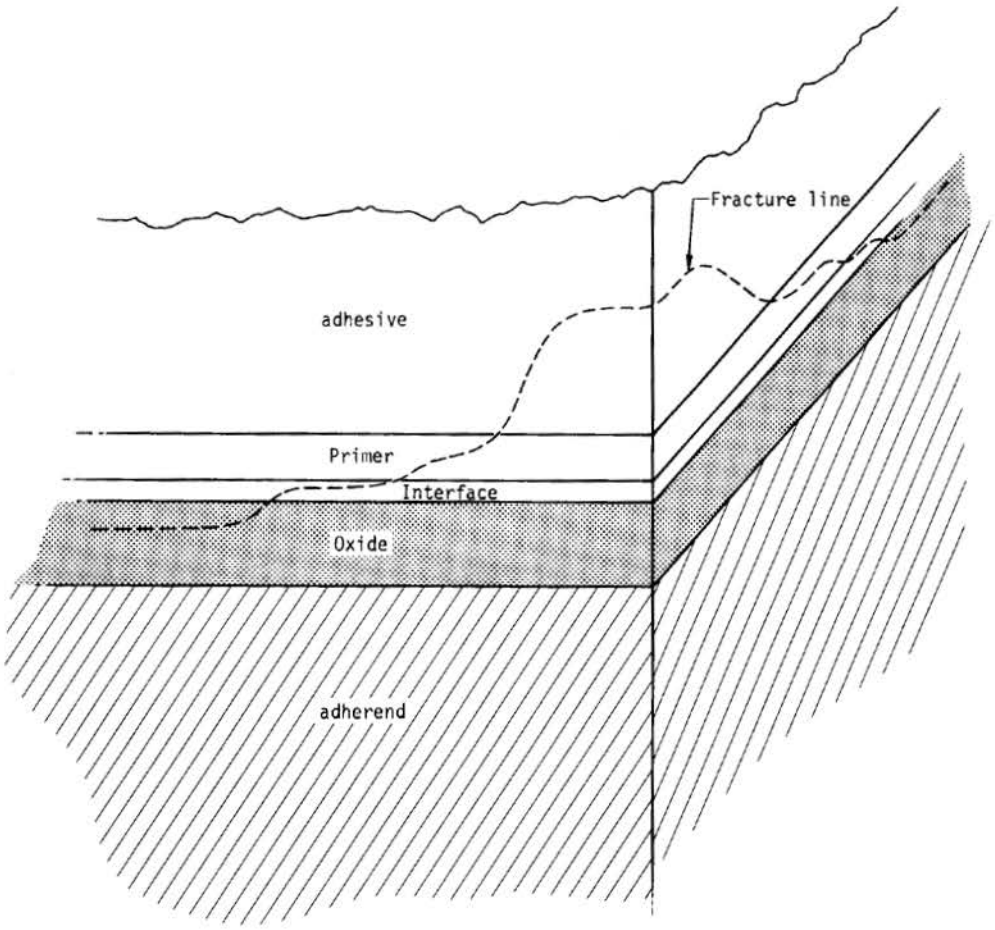


Fig. 1. Schematic representation of a bond line.

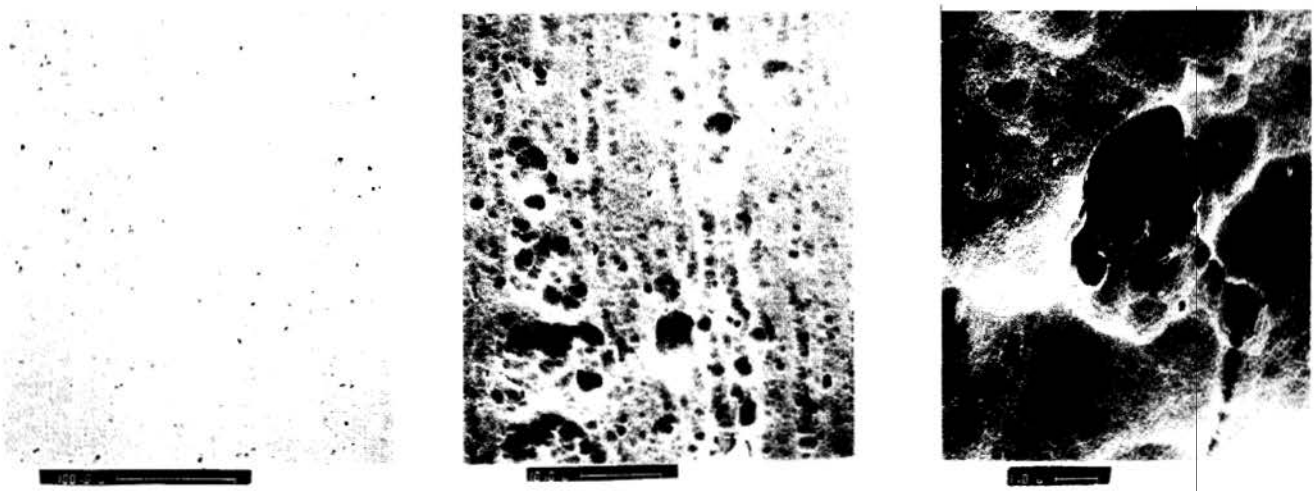


Fig. 2. Scanning electron micrographs (SEM) of a FPL etched Al 2024-T3 surface.

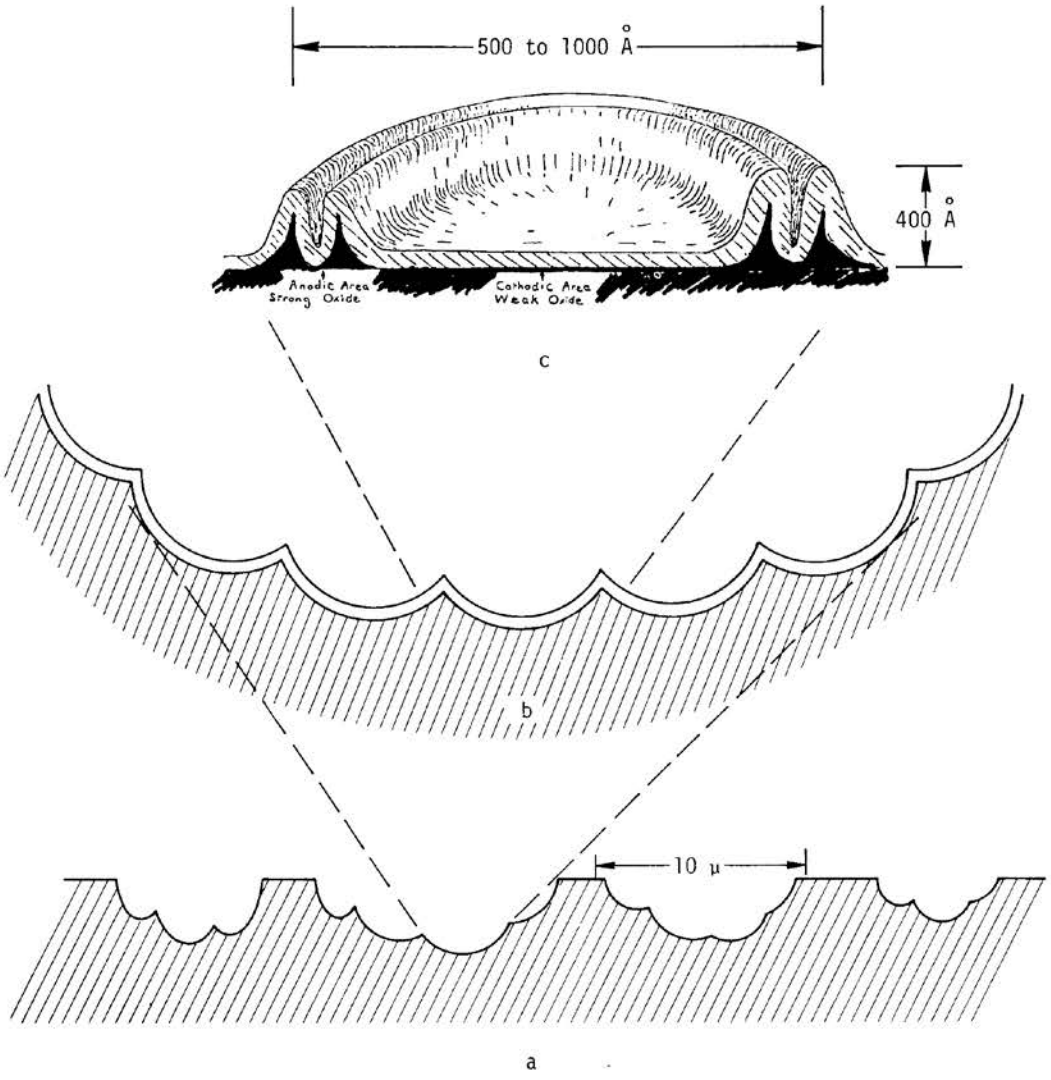


Fig. 3. Schematic representation of FPL etched aluminum at three magnifications.

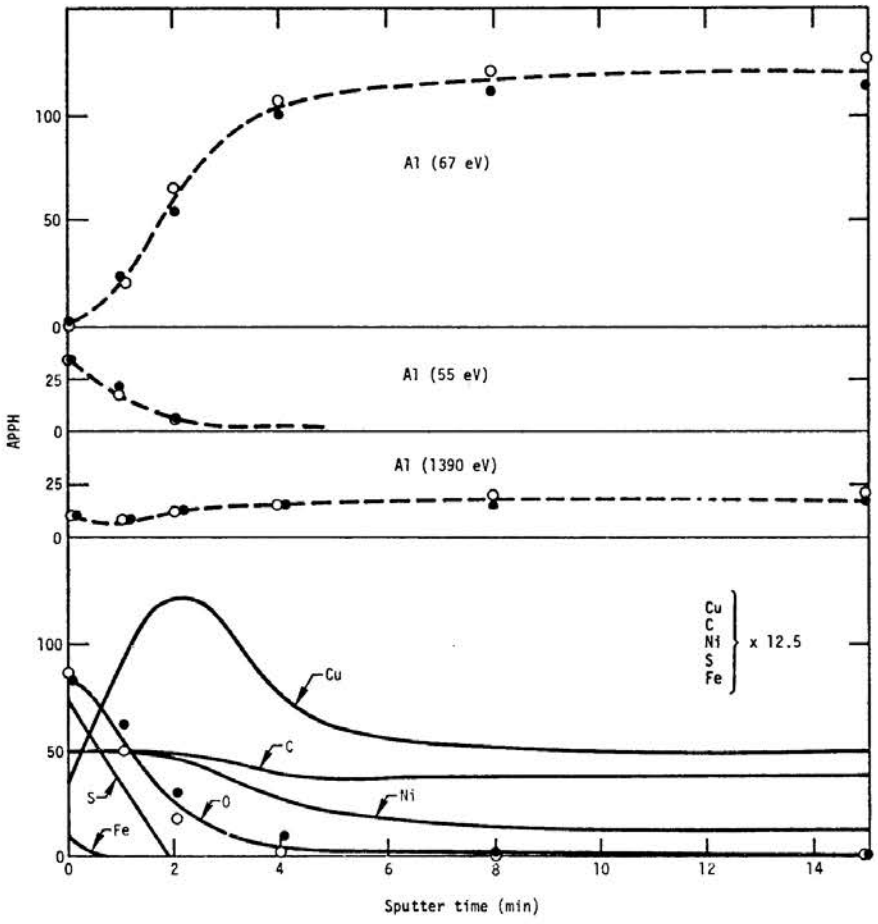


Fig. 4. Chemical profiles of Al 2024-T3 films formed by the dichromate surface treatment. APPH stands for Auger peak to peak height of the dN(E)dE vs E spectrogram. The open and closed circles are for duplicate samples.

mum as the film is transversed. This gives us some idea of the chemical constituents of the oxide film as you look through that film.

If you make bonds in a standard single overlap-joint and age at 100% relative humidity, you see in Fig. 5 that failure is essentially at the interface between the primer and the metal. Ellipsometry shows that the oxide film has actually grown from about 100 Å up to about 500 or 600 Å thick. The weakness in the oxide has allowed it to fail in the oxide itself. On the other hand, if you age at 95% relative humidity, rather than 100%, failure will occur in the various areas mentioned.

In Fig. 6 the glass carrier has split through the middle, leaving glass fibers on both sides. The dark areas in Fig. 6 failed at the interface and the lighter areas show the adhesive surface at the other interface; but you will also notice there is some cohesive failure. The most informative picture is Fig. 7 where cohesive failure and cavities are observed. The adhesive, during cure, produces water vapor which causes bubbles to form within the glass networks. A schematic of this type of bond is given in Fig. 8 which shows metal, adhesive with glass and void areas caused by the bubbling of the water vapor. When the bond is fractured it may fracture along the interface itself, but if it fractures in the adhesive, it will fracture across glass bundles of fibers and also cohesively across the adhesive as well as across void areas in between.

The total bond strength is a composite of all of the strengths that are in the various areas. If you make the over-simplication that the bonds in various regions are in parallel, the total bond strength σ_b, will be the sum of the fraction of the area that failed interfacially, ϕ_I, multipled by the intrinsic bond strength of that area, σ_I, plus the fraction that failed cohesively, ϕ_c, times its bond strength, σ_c, plus the fraction that failed in the glass, ϕ_g, times its bond strength, σ_g.

$$\sigma_b \approx \phi_I \sigma_I + \phi_c \sigma_c + \phi_g \sigma_g. \tag{1}$$

The total of the fractions, of course, add up to one which now includes the void volume fraction, ϕ_v,

$$\phi_I + \phi_c + \phi_g + \phi_v = 1. \tag{2}$$

If you make the approximations that the strength of the glass is that of the adhesive and the void area is rather small, you obtain Eq. (3) which gives the total bond strength in terms of the fraction that failed cohesively and the intrinsic strengths.

$$\sigma_b \approx \phi_c (\sigma_c - \sigma_I) + \sigma_I \tag{3}$$

The fraction that failed cohesively is determined by a microscopic examination with a grid system. A plot of σ_b vs. ϕ_c is given in Fig. 9, which shows that

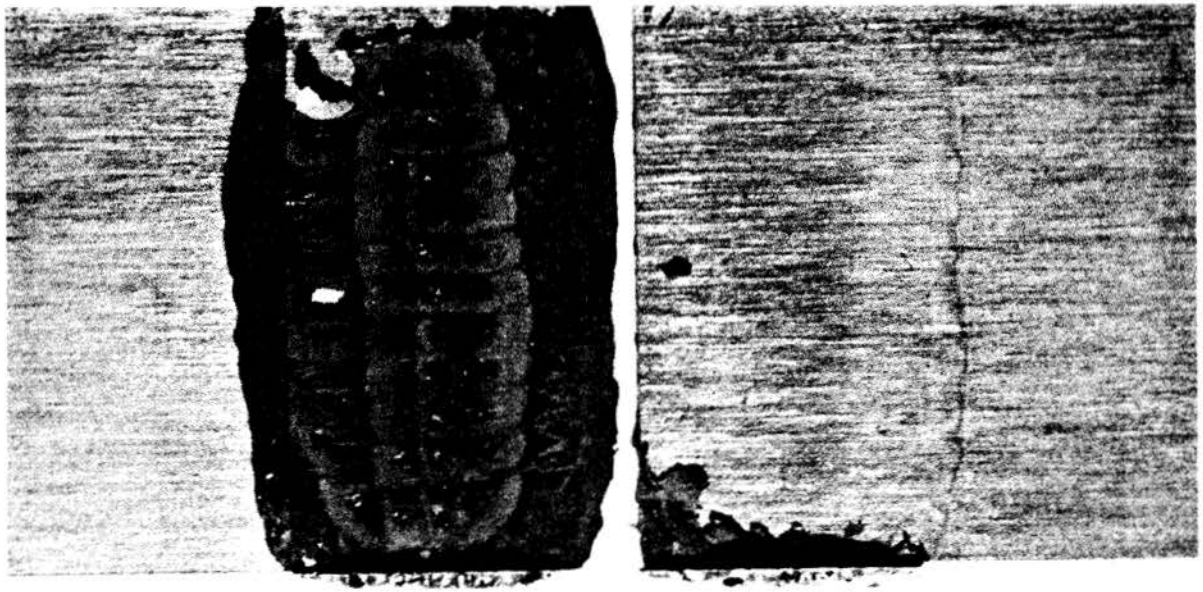


Fig. 5. Photograph of fractured bonds for Al 2024-T3 - HT424 after aging at 54°C and ~ 100% R.H.

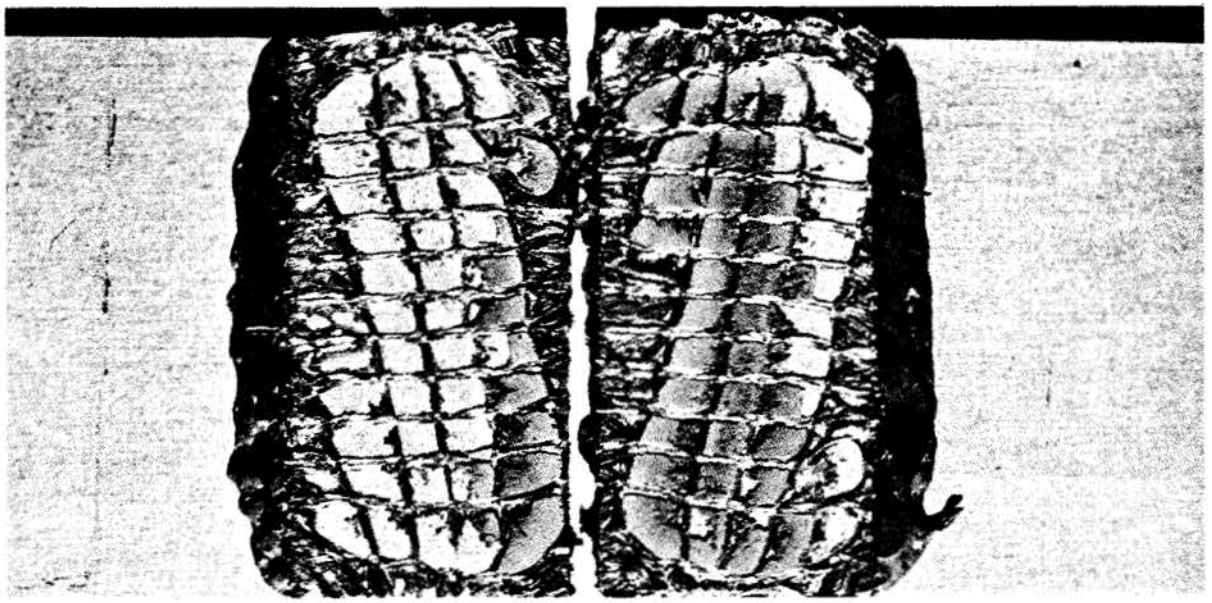
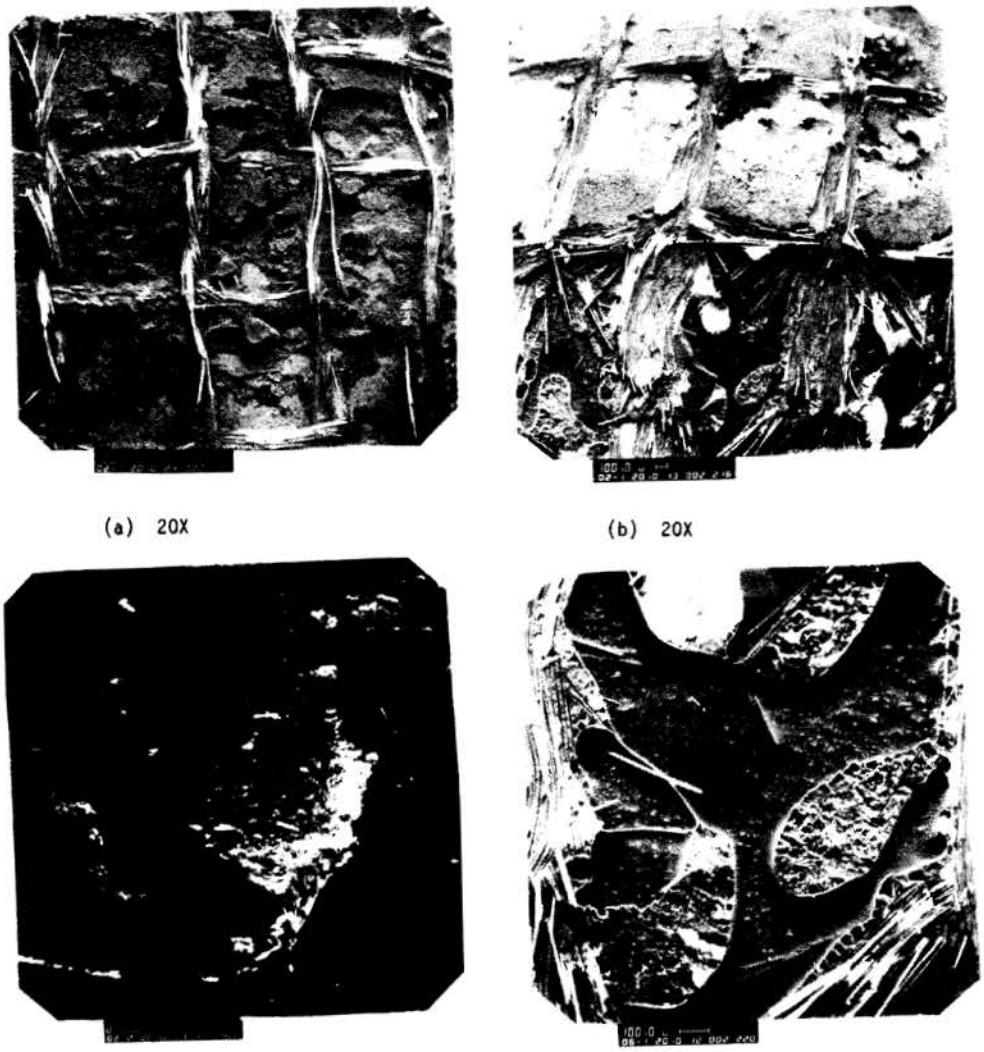


Fig. 6. Photograph of fractured bonds for Al 2024-T3 HT424 joint after 808 hours at 54°C and 95% R.H.



(a) 20X (b) 20X

(c) 200X (d) 60X

Fig. 7. SEM micrographs of an Al 2024-T3 - HT424 joint after fracture. SET = 0, BET = 0.

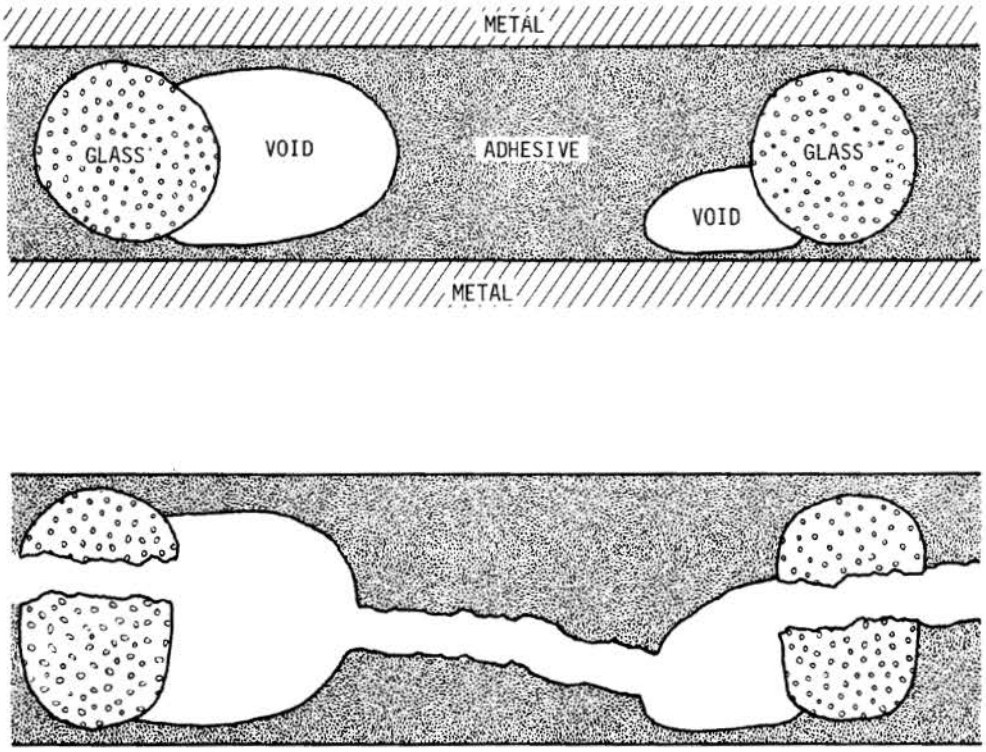


Fig. 8. Schematic representation of an adhesive bond before (top) and after (bottom) cohesive fracture.

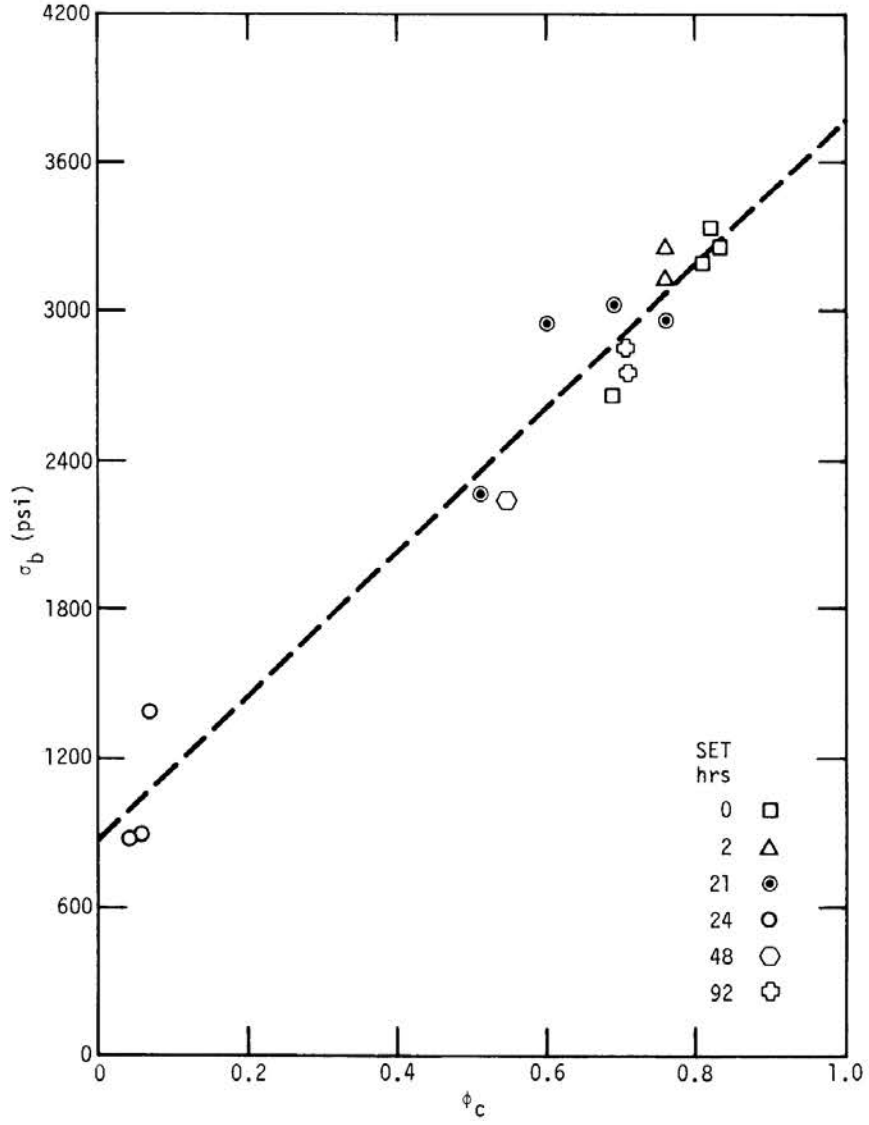


Fig. 9. Plot of σ_b vs ϕ_c for various SET.

in certain cases the approximation is not too bad. The intercept of the line in Fig. 9 at $\phi_c = 0$ gives σ_I about 800 psi and the intercept for cohesive failure, $\phi_c = 1$, gives $\sigma_c \approx 3800$ psi, which is that reported by the manufacturer as the strength of the adhesive. I point out that if you make bond strength studies, and you just measure the σ_b, the total bond strength, correlation with properties or system parameters such as humidity or temperature or whatever, it's not going to be productive until you have been able to separate σ_I, σ_c, and the ϕ values. Once a set of values of σ_I has been obtained as a function of temperature or humidity, etc. they can be related to the physical and chemical properties of a particular region.

Now, let us consider the effect of physical and chemical surface properties on bond strength. Table I gives data for three surface treatments: degrease, FPL etch, and plasma clean. After these surface treatments, the oxide thicknesses are 200,100 and 200 Å respectively. The surface potential difference is 0.5 and 0.48; so, there's really no difference to speak of. Measuring the roughness of the surface with a light scattering technique, yields about $0.2\mu_m$ as an rms roughness in the vertical direction for the first two treatments. The plasma treatment was not measured but should be about the same. The right of Table I shows the degreased sample to yield at 2367 psi as compared to 3000 for the other two. What has caused the almost 800 psi decrease for the degreased sample as compared to the others? The thickness of the film does not correlate with strength, the surface potential doesn't, and the roughness doesn't, whereas the Auger spectroscopy does. For the degreased sample, the carbon peak is very large and silicon and chlorine are present, whereas the other samples do not have any of these contaminants to speak of. The contamination is probably not much more than a monolayer after the degrease process but has caused the contact angle for water to be 130° as compared to approximately 0° for the other two techniques. We come to the conclusion that the cause of the bond degradation for the degreased samples is due to a monolayer or so of low energy material on the surface which has degraded the surface energy, and, therefore, the wetability properties of the surface.

Table I. Surface Character and Bond Strength

Surface Treatment	Oxide Thickness	SPD	rms Roughness	AES			Contact Angle	Strength
				C	Si	Cl		
	(Å)	volts	μ				deg.	psi
Degrease	200	0.50	0.2	65	14	12	130	2367
FPL	100	0.48	0.2	0.5	0	0	4	3080
Plasma	200	--	--	--	-	-	0	3130

DISCUSSION

MR. STUHRKE (Martin-Marietta): First, I want to compliment you on a beautiful piece of work. Have you presented this in any other reports that I can get?

DR. SMITH: Yes, Air Force Report AFML-TR-74-73.

DR. ROBB THOMSON (National Bureau of Standards): I'm a little puzzled that you can simply take a volume fraction of each failure strength, and then that's the total failure strength of the material, because if you've got a mixture of fairly ductile material like a polymer and a highly brittle material like the glass I would imagine that those would fail at different times. Now, this is not to say that the stress is not carried while the glass is failing partly by the polymer, but I wouldn't imagine that the ultimate strengths would be simply a linear combination like that.

DR. SMITH: It is a gross assumption, but it's not as bad as it may appear. For example, if you considered a system of parallel bonds with different strengths, as long as it hasn't begun to fail, the total strength is going to be the sum of all of the bonds regardless of whether one bond is weaker than the other. Once it starts to fail, the whole thing falls apart.

DR. THOMSON: Yes, this is true for the elastic part of it, but my question is was the ultimate strength --to say that the ultimate strengths are summable in that way doesn't seem to be a very good approximation.

DR. SMITH: For our experiments the stress strain curves were linear almost to failure.

PROF. HARRY TIERSTEN(Rensselaer Polytechnical Institute): Is it the polar or shear?

DR. SMITH: It's a standard lap shear test. The values that I'm talking about are the values of the stress at failure.

PROF. TIERSTEN: Do you know anything about the ductility of the material?

DR. SMITH: No. You might talk to Dave Kaelble about the properties of the adhesive.

PROF. TIERSTEN: Because according to elasticity you would get very high stresses at the end in a piece of bonded aluminum.

DR. SMITH: Yes, it's a complicated system.

PROF. TIERSTEN: And that would be unusual then.

DR. SMITH: The plot that I showed is certainly based on a gross assumption, I agree. The actual fracture analysis of it is much more complicated than I'm talking about.